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The Drop-Weight Method for the Determination of Surface Tension

A DISSERTATION

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SUBMITTED TO THE FACULTY OF THE OGDEN GRADUATE SCHOOL OF SCIENCE IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

By Edmund Charles Humphery

EASTON, PA.:
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THE DROP-WEIGHT METHOD FOR THE DETERMINATION OF SURFACE TENSION.[1]

(SURFACE TENSION I.)

The two methods in most general use for the determination of the capillary constants of liquids are the capillary tube and the drop weight methods. Of these two, the first is much the more sensitive to the action of impurities, since the surface of the liquid involved in the measurement is made very small, while in the drop weight method the surface is not only made relatively large but it is also renewed much more easily. It is not surprising, therefore, that the most concordant results on the surface tension of a single liquid are obtained by the drop weight method, and that duplicates run by this method, when it is properly applied, show a most remarkable agreement. However, when the results obtained by different workers on different liquids by this method are compared with determinations made by other methods, it is found that they show just as remarkable a disagreement, the deviation in some cases rising to 20%, or even 40%. These very bad results are due however, not to any inherent fault in the method, but to the application of a very faulty theory. Thus many workers have used the equation

$$W = 2\pi r\alpha, \qquad (1)$$

where W is the weight of the drop, r the radius of the tip of the dropping tube, and α the surface tension. This equation would be true only when the pendant drop is supported entirely by the surface tension of the surface film at the edge of the tip, and when all of the pendant drop falls, but this is very far from the truth, for the drop which falls is nowhere nearly all of the pendant drop.

The most complete treatment of the mathematical theory of the relation between the forms of drops and surface tension is given in a book published in 1883 by Bashforth and Adams.[2] Much later than this, in 1906, Lohnstein[3] applied the general theory to the special case of the hanging drop just before its fall, and the residue left after the fall, and from the difference he obtained the magnitude of the falling drop itself. By doing

[1] Read before the National Academy of Sciences, December 7, 1914.

[2] "Capillary Action," Cambridge University Press (1883).

[3] *Ann. Physik*, [4] **20**, 237–68, 606–18(1906); *Z. physik. Chem.*, **64**, 686 (1908); **84**, 410 (1913.)

this he was able to reduce the problem, which would otherwise be of a kinetic form, to the solution of problems in statics. In solving the problem it was necessary for Lohnstein to make an assumption in regard to a relationship between the form of the drop just before it falls, and that of the residual drop left immediately after the fall. The cross sections of the drop as it increases in size give a family of curves which have different values of a variable parameter. Two values of this parameter give two curves which have the same tangent at the point of contact with the tip. Lohnstein assumed that the drop which remained after the fall had a cross section which gave a curve with the same angle of contact with the tip as the drop just before it fell. In calculating the size of the falling drop, then, he subtracted the volume of the drop with the parameter p from the volume of the drop with the parameter p', where the two curves, due to these different parameters, have the same tangent at the point in which the drop meets the tip. The curve with the parameter p' gives the form of the drop before the fall, and the curve with the parameter p gives the form of the drop remaining after the fall.

The equation obtained by Lohnstein for the weight of the falling drop is

$$W = 2\pi r\alpha f(r/a), \qquad (2)$$

where r is the radius of the tip and a is the square root of the capillary constant, and $f(r/a)$ represents a function of r/a. The surface tension is given by the equation

$$\alpha = W/2\pi r f(r/a), \qquad (3)$$

and since $f(r/a)$ varies from 1.0 to 0.6, it is evident that results obtained by the older equation (1) may be increased by as much as 65% by the application of this correction. Lohnstein determined the values of the function of r/a for different values of r/a, and his calculation of these corrections from a theoretical standpoint makes it possible to use the drop weight method for the determination of surface tension, and, since, as has been stated, this is the most exact from an experimental standpoint of the methods used in work on capillarity, Lohnstein's work represents a great advance in our knowledge of this fundamental subject.

Unfortunately, however, when it becomes desirable to determine the surface tension by this method, it is found that Lohnstein did not carry his calculations of these corrections to a sufficient degree of accuracy to make this method available for determinations where an accuracy greater than 4% is desired. It is therefore important that this correction, which is a very fundamental one in work on capillarity, should be determined with a greater degree of accuracy. For this purpose the apparatus devised by the writers[1] seemed to make it possible to make determina-

[1] Described in the paper which follows.

tions of this correction under conditions which are more nearly ideal than is possible by the ordinary methods. Thus the substitution of work on the liquid-liquid interface for the ordinary method in which a liquid-air interface is used makes it possible to compare the drop weight results with those obtained in a capillary tube of large bore (1.4 mm.) when the capillary rise is great enough (78.0 mm.) to give accurate measurements. Not only can the diameter of the large capillary be determined more accurately than that of the smaller tube used for measurements on a single liquid, but in addition it is much easier in the large tube to keep the surface of the meniscus in a pure condition. Then in the drop weight determination itself, the drop falls very much more slowly when it falls into a liquid than when it falls into a gas, so that there is less disturbance in the drop at the time of fall than when it breaks away at a relatively high speed. The corrections determined in this way are given in Table I, and are

TABLE I.—EXPERIMENTAL CORRECTION FOR DROP WEIGHTS.

Point No.	r/a.	$f(r/a)$.	Interface.	Temperature.
1	0.281	0.709	Water—Ethyl carbonate	(25°)
2	0.366	0.685	Water—Benzene S. T.	(25°)
3	0.441	0.672	Water—Dimethylaniline	(25°)
4	0.484	0.654	Water—$EtCO_3$	(25°)
5	0.592	0.639	Water—Benzene	(10°)
6	0.621	0.636	Water—Benzene	(20°)
7	0.633	0.632	Water—Xylene	(25°)
8	0.636	0.634	Water—Benzene	(25°)
9	0.648	0.634	Water—Benzene	(30°)
10	0.649	0.632	Water—Toluene	(25°)
11	0.709	0.620	Water—Air	(25°)
12	0.837	0.615	Water—Hexane	(25°)
13	0.845	0.616	NaCl Soln.—Benzene	(25°)
14	1.071	0.612	Benzene—Air	(25°)
15	1.387	0.620	$SrBr_2$ Soln.—Hexane	(25°)

shown in the form of a curve in Fig. 1. In the figure the ordinates represent the values of the function of r/a, and the abscissae give the values of r/a. The circles which are inked in represent Lohnstein's theoretically determined values, while the circles given in outline give the new values determined experimentally. The figure shows that the experimental values give with Lohnstein's first two points for small values of r/a, a much smoother curve than is given by his own theoretical values. The experimental values were determined by the use of a number of different liquids, and measurements were made both upon liquid interfaces, and at the surface of a single liquid. Table II gives a list of the corrections for round values of r/a.

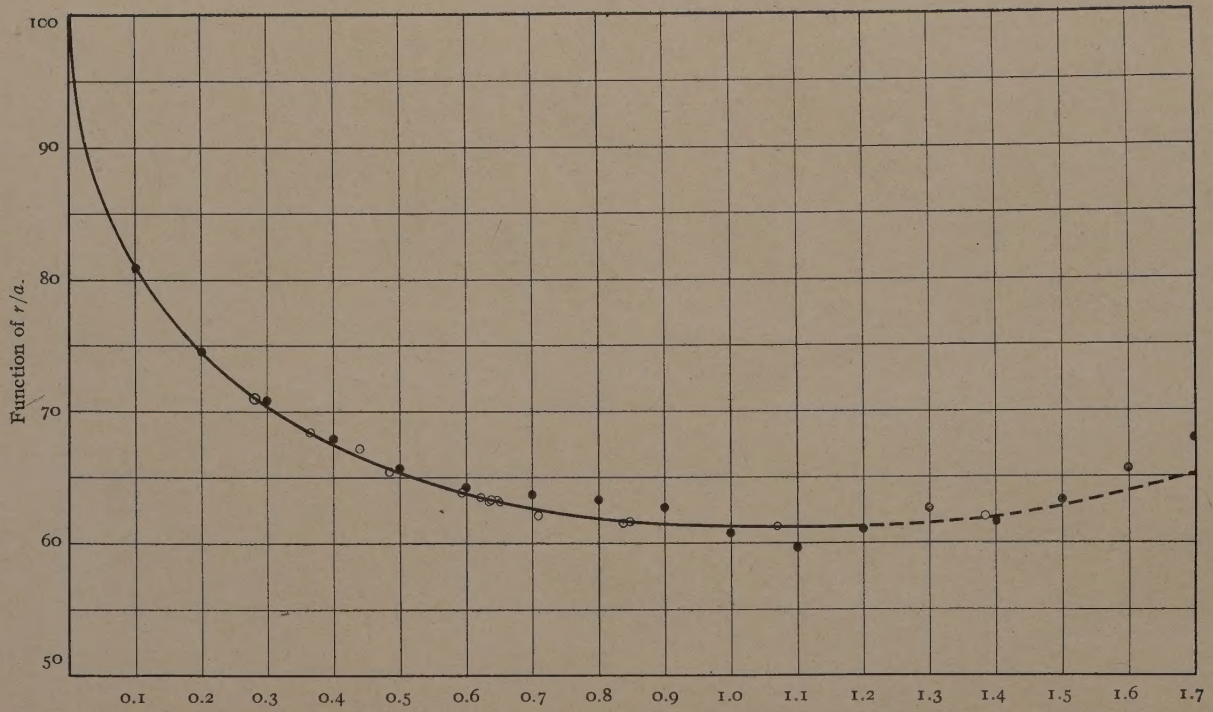

Fig. 1.—Experimental determination of the corrections for the drop-weight method of determining surface tension. Preliminary determination accurate between $r/a = 0.3$ and $r/a = 0.7$. Experimental values = circles in outline. Lohnstein's values = circles inked in.

TABLE II.—CORRECTIONS FOR DROP WEIGHT—FROM CURVE.

r/a.	$f(r/a)$.	r/a.	$f(r/a)$.
0.0	1.000	...	...
0.1	0.805	0.9	0.614
0.2	0.741	1.0	0.612
0.3	0.703	1.1	0.612
0.4	0.676	1.2	0.613
0.5	0.655	1.3	0.615
0.6	0.637	1.4	0.620
0.7	0.625	1.5	0.629
0.8	0.618 See note (1)	1.6	0.641

The correspondence between the experimental results and the smooth curve drawn through Lohnstein's first two points, and the additional fact that the experimental curve follows the general trend of Lohnstein's values, shows that the relationship thus developed theoretically by Lohnstein must be, on the whole, the correct one. However, some prominent workers on surface tension still refuse to accept the validity of Lohnstein's work and prefer to use in place of his relationship the so-called law of Tate. The law of Tate states that the weight of a drop falling from a tube is proportional to the radius of the tube and to the surface tension of the liquid. Thus Morgan, in a paper printed in 1915 and entitled "Das Tatesche Gesetz, Eine Antwort an Herrn Lohnstein," states as the conclusion of one of his sentences

"Man muss folgern, dass die form des Tateschen Gesetzes $\gamma = Kw$ für die benutzten Mundstücke ein wahres und strenges Gesetz ist."

If Tate's law holds the ratio $\frac{\text{Drop weight}}{\text{Tip diameter}} = K.$

Morgan gives the results of work upon 16 tips varying in diameter from 3.05 to 7.86 mm. in confirmation of this law. In order to see the relation of this work to the experimental correction curve, the corrections have been calculated from Morgan's values (Table III) and plotted in Fig. 2. Morgan has not, in any of these cases, determined the absolute surface tension himself, since his work gives only relative values, so the vertical position of his curves as a whole is dependent upon the value which he chooses as the surface tension of his standard liquid. Now the values of these surface tensions are taken from the work of others, and are usually the result of work by the capillary tube method. It is therefore evident that the curves representing Morgan's work as given in

[1] For values of r/a greater than 0.7 the values are only approximate, since enough determinations have not been made in this region to fix these values with certainty. The indications are that if any change is shown by further experiments the change will be such as to *decrease* the values here given. They already represent a considerable *decrease* in comparison with the results obtained by Morgan, when he uses the work of Ramsay and Shields and other investigators in order to obtain the constant in this equation.

TABLE III.—CALCULATION OF $f(r/a)$ FROM MORGAN'S RESULTS.

Benzene. S. T. = 26.92. t = 27.8. d = 0.87059. a = 2.5117.		Quinoline. S. T. = 42.66. d = 1.08755. a = 2.829.		Pyridine. S. T. = 35.33. d = 0.97365. a = 2.708.		Carbon tetrachloride. S. T. = 24.89. d = 1.57528. a = 1.795.		Ether. S. T. = 15.33. d = 0.7045. a = 2.107.	
r/a.	$f(r/a)$.	r/a.	$f(r/a)$.	r/a.	$f(r/a)$.	r/a.	$f(r/a)$.	r/a.	$f(r/a)$.
0.607	0.6595	0.539	0.673	0.5605	0.6573	0.8494	0.6377	0.7238	0.6569
0.782	0.636	0.6946	0.6434	0.7222	0.6425	1.095	0.6273	0.9326	0.636
0.796	0.6356	0.707	0.643	0.7355	0.636	1.114	0.6268	0.9749	0.6359
0.8978	0.6237	0.797	0.624	0.8288	0.623	1.256	0.6237	1.070	0.6234
0.9356	0.6226	0.880	0.624	0.915	0.623	1.309	0.6275	1.182	0.623
0.9913	0.6227	0.972	0.624	1.011	0.6225	1.387	0.631	1.305	0.6227
1.057	0.6227	1.006	0.624	1.022	0.622	1.479	0.6376	1.350	0.626
1.095	0.6223	1.034	0.6213	1.075	0.622	1.532	0.643	1.388	0.6264
1.133	0.622	1.096	0.6215	1.204	0.622	1.585	0.651	1.554	0.642
1.165	0.621	1.158	0.622	1.257	0.6224	1.639	0.658	1.623	0.647
1.234	0.6223	1.209	0.6214	1.352	0.6257	1.727	0.660	1.754	0.6613
1.304	0.6256	1.306	0.6248	1.444	0.630	1.824	0.6636	1.865	0.6757
1.362	0.6297	1.392	0.6294	.....	.....	1.905	0.671	.....	.....
1.471	0.639	.....	.....	.....	.....	.....	.....	.....	.....
1.565	0.6465	.....	.....	.....	.....	.....	.....	.....	.....

Fig. 2 may be brought down to the same general level as the experimental correction curve, but the curves cannot be made coincident. The law of Tate might be said to hold over the region where the correction curve is horizontal, but this is the case only where the curve and its horizontal tangent become the same. This is not strictly the case for any part of the correction curve, but when the corrections are determined from Morgan's work it is seen that a large number of the points do lie on a straight horizontal line; on the other hand a large number of points lie very far from this straight line. In comparing the two results it should be remembered that the lower the correction factor, and therefore the lower the curve, the higher the surface tension, so that values obtained from the correction curve determined by the writers would be higher than those corresponding to Morgan's values.[1]

[1] That our *lower* values for the correction factor, that is, the *higher* values for surface tension are more apt to be the better, is confirmed by the recent work of Richards and Coombs, THIS JOURNAL, July, 1915, who obtain surface-tension values for benzene which are considerably higher than those found by the capillary-tube method by Ramsay and Shields, Renard and Guye, and Walden and Swinne. The deviation is of the order of 3%. The fact that Morgan's results give a higher correction factor than ours does not mean, therefore, that his drop weights are as a whole too low, but it indicates that the capillary-height method has in the past given results which are in general too low, for Morgan has not used any capillary-height measurements of his own, but seems to have determined the constant of his equation from the average capillary height determinations of other investigators. The discrepancy is therefore due, in all probability, to errors in the capillary-height methods and, not to deviations in the weights of the drops themselves.

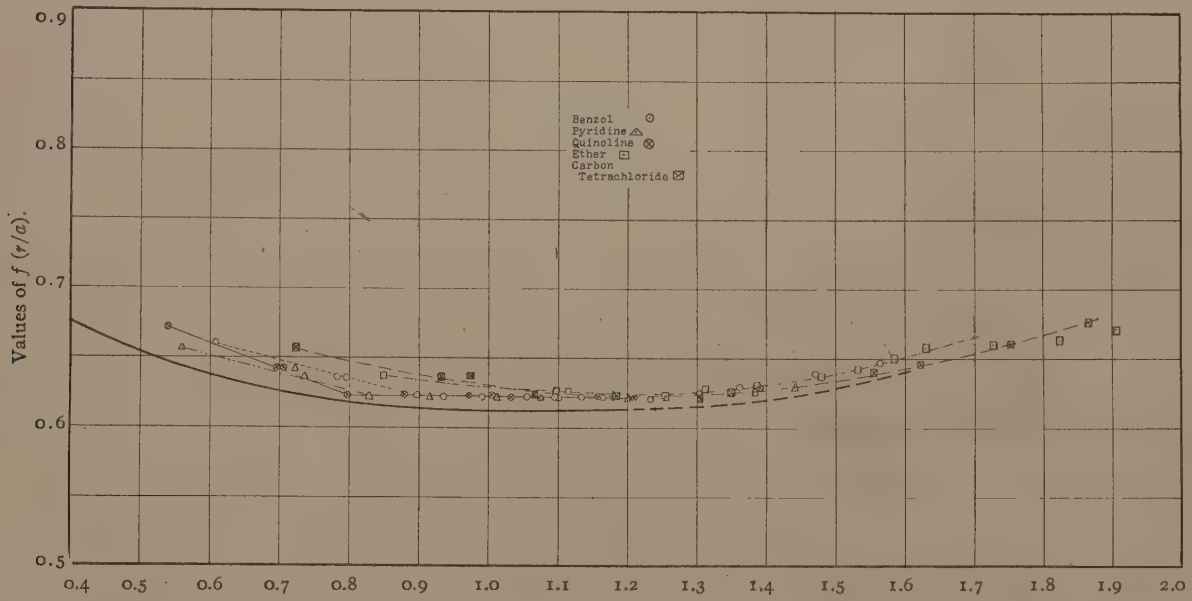

Fig. 2.—Values of the drop-weight correction calculated from Morgan's work with the theoretical curve given below for comparison.

Such great care has been taken by Morgan in his work that it would seem worth while to endeavor to find a cause for the fact that the correction curve determined by us is so closely in accord with Lohnstein's theoretical work, and that the values given by Morgan for small values of r/a deviate so widely from the general form of the correction curve. This work is now being done by Mr. E. D. Wilson in this laboratory. He is beginning the work with the aim of making more complete calculations than those of Lohnstein, and at the same time to introduce into the equations such factors as viscosity, in order to see what would be the result of variations in these properties. The deviations in Morgan's work do not follow the order which would be given them by a variation of any one of the following properties of the liquids: viscosity, vapor pressure, density; but it is of course possible that more than one of these may be effective at the same time. The effect of differences of vapor pressure in changing the volatility of the liquid should not enter into the equations, since such effects should be eliminated by the experimental methods.

The use of very small tips makes the value of the function of r/a approach the value one, but the slope of the curve for these very small values of r/a is so great that it is difficult to tell exactly what correction to apply. This is illustrated by the irregularity in the corrected results of Antonow on the surface tension at the interface water-benzene, as given in Table IV, where the variation amounts to 8% of the maximum value.

TABLE IV.—ANTONOW'S DETERMINATIONS OF THE SURFACE TENSION AT THE BENZENE-WATER INTERFACE BY THE USE OF EXTREMELY SMALL TIPS.

Radius in mm.....	0.13	0.175	0.350	0.630
$\alpha_{18°}$ corrected.....	34.93	36.04	37.97	35.40

The value obtained by the writers with larger tips is 34.18 dynes.

The correction curve is now most accurately known between the values of r/a from 0.3 to 0.8, since that is the more common range for the tips which have been available for work on the liquid-liquid interface. Seven new tips are now available for use and the corrections from 0.8 to larger values of r/a will be made more accurate by further work.

The writers wish to express their indebtedness to the American Academy of Sciences, Arts, and Letters for a grant of three hundred dollars from the C. M. Warren Fund. The grant will be used in a continuation of this research. The work described in papers II, III, and IV of this series has been accomplished by the use of this fund.

APPARATUS FOR THE DETERMINATION OF THE SURFACE TENSION AT THE INTERFACE BETWEEN TWO LIQUIDS.

(SURFACE TENSION II.)

The surface tension at the interface between two liquids has been determined by a number of different methods,[1] but of these only two, the method of the falling drop, and the capillary-tube method, seem well adapted for general use. The importance of the interfacial tension in work in colloidal chemistry and in biological research, makes it essential that the apparatus for the determination of the surface tension should be of better design than that which has been used in most of the research work on this subject.

The Drop-Weight Apparatus.

The most essential features of a drop-weight apparatus are that the tip shall be ground almost perfectly round, with very sharp edges, and that the diameter of the tip shall be of the proper magnitude to give a ratio between the radius of the tip (r) and (a) the square root of the capillary constant, such that the Lohnstein correction[2] for the particular value of r/a may be one which has been accurately determined, and also such that this correction shall not vary rapidly with the radius. The neglect of these essential conditions has been so general that this method in practically all of the previous work on interfacial tension has been very inaccurate. Thus Antonow in his fundamental work on the relation between the tension at the interface and that of the separate phases, evidently in the endeavor to make the correction factor close to unity, chose tips with very small diameters. This does, as a matter of fact, make the factor much closer to unity than if larger tips were to be used, but it also makes the correction vary greatly as the value of r/a changes. Thus the correction factor changes its value from 1.000 for $r/a = 0$ to 0.741 for $r/a = 0.2$, or a variation of 25.9% over a range of 0.2. On the other hand, when larger tips are taken a variation of r/a from 0.9 to 1.2 changes the correction by only 0.2% as a maximum for a change of 0.3 in the values of r/a. For dropping water into other liquids the tip which has been used

[1] For a critical account of twenty methods see "A critical paper by Ferguson," *Science Progress*, Jan., 1915, p. 428.

[2] For an explanation of the Lohnstein correction see the paper which precedes this one.

most largely has a diameter of 9.5 mm., which is very satisfactory, though when dropping water downward into other liquids, the diameter should be somewhat greater if it is desired that the correction factor shall be as constant as possible for different liquids. This is, however, not necessary, since the correction curve has a slight slope and is well determined in the range where this tip is used.

The apparatus, but not its supporting stand, is shown in Fig. 3. It consists of a pipet of a capacity of 10 cc. which for convenience should be made smaller if much smaller drops are to be obtained, either on account of the use of a smaller tip, or because of a greater difference of density between the two liquids. Above and below the bulb of the pipet the stem is graduated to 0.1 cc. so that readings may be made to 0.01 cc. In order to give a better control of the drop the long vertical capillary tube at the right is made as small as a diameter of 0.3 mm.

The short arm H at the right which has the tip at its lower end is sealed into a large glass stopper, E. The glass beaker F, which is used to hold the lighter liquid, is fastened to the glass stopper by means of a ground joint which is made with a very slight slope, and a longer line of contact than is shown in the figure. The apparatus is supported by a thick sheet of aluminium used as a back, and on the top of this rests a platform which supports a level. The level is set on adjusting screws, so that the end of the tip may be set horizontal. The back and the platform are supported by heavy horizontal rods which are clamped to a vertical 30 mm rod. This is fitted into a heavy tripod with three leveling screws.

The lighter of the two liquids used in the determination is not usually put directly into the beaker F but into a smaller glass cylinder which rests on the bottom of the beaker, since the beaker is so large that it requires a large amount of liquid. The apparatus is supported in a thermostat with the water level at L. The tube G is used to connect the beaker with the apparatus used for the production of a sufficient decrease of pressure so that the drop may be drawn over. This apparatus, while extremely simple, should be such as to give perfect control of the drop. It consists of a buret with two connecting tubes sealed on at the top. Each of these connecting tubes is fitted with a glass stopcock.[1]

The procedure used in making the determination is to first fill the pipet by suction until the liquid rises to the 0.2 or 0.3 mark on the upper graduation, the liquid is then allowed to run out until it stands at about the 0.0 cc. mark, when a clamp on the rubber tube fastened on the glass tube at A, is closed.

[1] For a description of this apparatus see paper by Harkins and Brown, *J. Am. Chem. Soc.*, 38, 250 (1916).

Then the cylinder containing the lighter liquid is adjusted in the beaker F and the metal shelf on which the beaker rests is lifted to hold it. Care should be taken that a sufficient amount of the liquid is used to raise its level about 1 cm. above the lower edge of the tip when the beaker is placed in its final position.

The apparatus is then lowered into the thermostat, and allowed to stand from 35 to 50 minutes before beginning the run. When the liquids have come to constant temperature the clamp at A is opened and the heavier liquid sucked back into the pipet until its surface is just beginning to enter the mouth of the tip. The height of the liquid in the upper graduated tube is read off. The tube G is then connected by a rubber tube with the suction apparatus, which is filled with mercury, and enough mercury is at once run out so that the drop will fall in from 3 to $3^1/_2$ minutes. This causes the drop to form rapidly at first, and with extreme slowness just before the drop falls. If it is seen toward the end of the formation of the drop that the suction is insufficient to cause it to fall, the stopcock at the bottom of the suction buret is rotated quickly, thus allowing a very small amount of mercury to escape. The tube at the bottom of this buret is drawn down to a capillary in order to help keep this amount of mercury small. These precautions are taken so that the liquid in the drop, just before its fall, may be as free from currents, and from motion as a whole, as is possible. It is, of

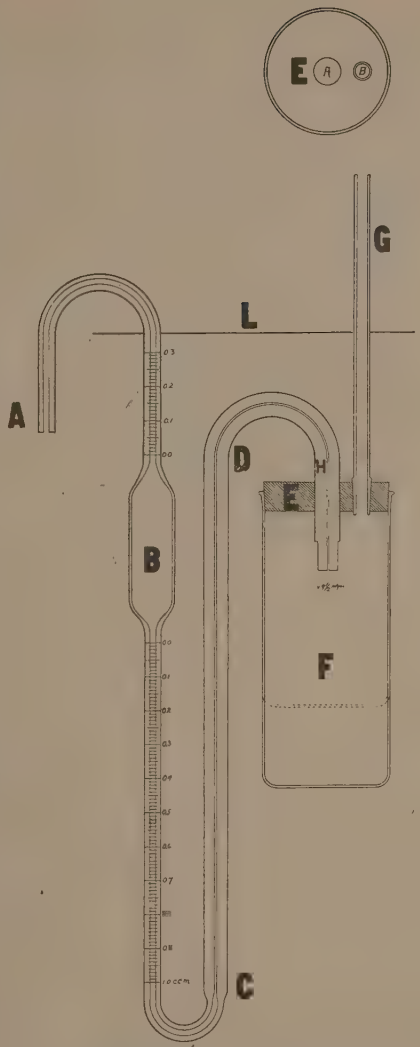

Fig. 3.—Glass parts of drop-weight apparatus, for determinations at a liquid-liquid interface.

course, impossible to reduce the actual dropping of the drop to a static phenomenon.

As soon as the liquid in the pipet falls until its upper surface stands in the lower graduated tube, it is drawn back until it again just begins to enter the mouth of the tip, and the final reading of volume is taken under the same conditions as at the beginning of the determination.

In order that the volume of the drop may be converted into its weight in the lighter liquid, the densities of both liquids must be determined with a degree of accuracy which should be increased as the two approach each other in density. For the more accurate determinations a new form of pycnometer was devised, and this will be described in a later paper.

Apparatus for the Determination of the Surface-Tension at the Interface between Two Liquids by the Capillary-Tube Method.

The apparatus used for the determination of the surface tension at the interface between two liquids by the capillary-tube method, is shown in Fig. 4*A*, *B*, and *C*. The base of the stand A is filled with lead so that it may rest upon a supporting pillar and still support the capillary tube

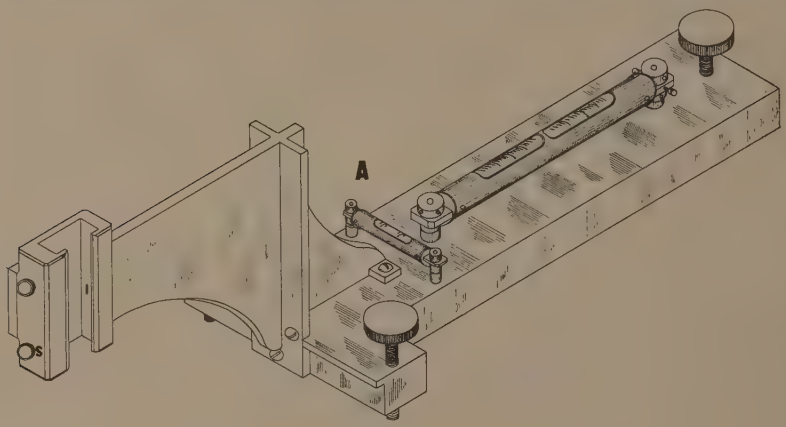

Fig. 4. .

in the thermostat. The stand is provided with levels which are adjusted so that when they are level the capillary tube is vertical. The capillary tube is made from Jena capillary tubing and fits through the holes D, D. Its top rests against the stop E. The top of the tube serves only as a support for the lower part and may therefore be replaced by a metal tube or rod. The support B is first fastened in its supporting stand at I, and is fastened by the set screws S, S, against I, which is ground so that both surfaces which come together at I are flat.

The procedure will be described for the case where water is taken as the heavier of the two liquids. In this case the tube C is filled with water until H is completely full and the bulb C[1] is also nearly full, but not so full that the large meniscus which forms strikes the top of this bulb. The capillary tube is steamed out for some time before it is used. This precaution, while seemingly very simple, is essential if the best results are to be obtained, since it puts the surface of the glass in a better condition than cleaning by a cleaning mixture, or the use of acids, alkalies, or organic solvents. Any of these may be used first if it is considered advisable. The capillary tube is then set into the tube M, and lowered by the ratchet screw R, until the top opening in the capillary is underneath the surface of the water, and all of the air is displaced by the water. The upper tubes are then filled with the lighter liquid (*e. g.*, benzene) and after the liquids come to the proper temperature in the thermostat, the capillary tube is raised until the water-benzene meniscus *falls* to one of the graduations on the tube. The point P, which is made of platinum and should be sharp, is lowered until it touches the mirror surface of the benzene-water interface in the bulb C. If the slides in B move with just the right amount of friction this adjustment may be made with extreme accuracy since the point P approaches its image in the interface and the moment the two touch, the water surface gives a slight jump upward. The vertical distance between the platinum point and the graduation on the tube may then be read off on the millimeter scale by means of the verniers, or a cathetometer may be used to determine the distance. The advantages in the use of this instrument are (1) that it holds the capillary tube firmly in a vertical position, and (2) that the ratchet screws allow the adjustment of the point P to be made with great ease, and also make it easy to lower the capillary tube into the water phase and then raise it until the meniscus is at one of the graduations on the tube. A cathetometer may, of course, be used to measure off directly the distance between the upper and the lower meniscus, and the work recorded here has been checked by measurements made in this way.

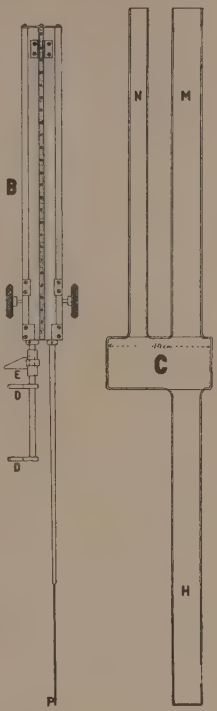

Fig. 4*B*. Fig. 4*C*.

The results obtained by the use of this method are much more concordant

[1] The bulb C is about 100 mm. in diameter, and has therefore a much larger free liquid surface than has been used in most other work on capillarity.

than the determinations made with a single liquid. This is due largely to the fact that with water-benzene a 1.4 mm. tube could be used and still give a capillary rise of 78 mm., while with water alone in a tube of 2.0 mm. diameter the rise was only about 14 mm., so that, where a considerable height of the capillary column is desirable, a much larger tube may be used for the determination of the interfacial tension. This is advantageous, since not only can the tube be cleaned more readily and the meniscus kept more free from those impurities which easily collect on a small surface and thus vitiate the results, but in addition the diameter of the tube can be determined more accurately.

The Standard Tube.

One difficulty in the determination of the surface tension of a single liquid by the capillary tube method is that the diameter of the tube must, in general, be determined by a mercury calibration, and this is unsatisfactory unless extreme care is taken in the selection of the capillary tube, since it is difficult to find a tube which has the same diameter at different points along its axis, so that the diameter determined by the calibration is usually not that of the tube at the point where the meniscus stands, and in addition the tubes are not round. Two methods of surmounting this difficulty suggested themselves: (1) to use in the place of the tube two plates of optical glass with flat surfaces practically parallel to each other; and (2) to enlarge the hole in a capillary tube by turning it out on a very accurate lathe, and thus make it practically round and of the same diameter for a distance of a few centimeters. This latter alternative, seemingly the more difficult of the two, is the only one which has been used up to the present time. The tube was made in a very skillful way by Captain A. de Khotinsky, the instrument maker for this laboratory, and by whom the eight tips used for the drop-weight method were ground. These tips are sharper and more nearly round than those which may be purchased from the makers of the Morgan drop-weight apparatus, which is, however, used for a different purpose than that described in this paper.

THE SURFACE TENSION AT THE INTERFACE BETWEEN TWO LIQUIDS, AND THE EFFECT OF ACIDS, SALTS AND BASES UPON THE INTERFACIAL TENSION.

(SURFACE TENSION III.)

Only a very few accurate measurements have been made upon the interfacial tension between two liquids. Table I gives the new results which have been obtained by the use of the capillary-tube method. The surface tension at the interface water-benzene between 0° and 40°, is given by the equation

$$\alpha = 35.54\ (1 - 0.056t).$$

The effect of acids, bases, and salts upon interfacial tension is of great interest on account of the importance of this effect in relation to colloids, and therefore it is also of great interest in the study of the physiology of plants and animals. It is well known that when a muscle is at rest it gives a neutral reaction, but when it becomes active the reaction changes to acid. One of the theories of muscular motion is that the production of carbonic, lactic, or other acids is caused by a partial decomposition of chemical compounds in the muscles, that this production of acid causes a change in the electromotive force between the fibrilles and the sarcoplasma, and that this in turn causes a change in the surface tension at the boundary between the two phases which is sufficient to account for the motion of the muscles. Experiments by Haber and Klemenciewicz show that this change of electromotive force, if produced in the system benzene–water, is of no small magnitude, but may be nearly as much as one volt for a small change of concentration from basic to acid near the neutral point. Although the relation between the chemical change and the electromotive force at the interface is thus very simple, the relations with surface tension are very much complicated and obscure. The

TABLE I.—SURFACE TENSIONS OF WATER—LIQUID X.

	Benzene.					Ethyl carbonate,	Dimethyl aniline.			
Liquid.	10°.	20°.	25°.	30°.	40°.	25°.		Xylene.	Toluene.	Hexane.
Surf. Tens. (Dynes)	34.98	34.52	34.18	33.82	33.22	13.00	25.78	37.60	36.10	49.54

effect of different concentrations of a number of acids, bases, and salts upon the interfacial tension benzene-water is shown by data given in Table II and in Fig. 5. As will be seen from this

table, the inorganic acids have only a small effect upon the interfacial tension, but the organic acids have a considerable effect, which increases with the change from formic toward butyric acid. The data are given for only one base, ammonium hydroxide. A large number of determinations have been made by the drop-weight method of the effect of highly ionized bases, such as sodium or potassium hydroxide. These bases lower the surface tension slightly, and the results obtained at any one time when the same solution of the base is used, agree well,

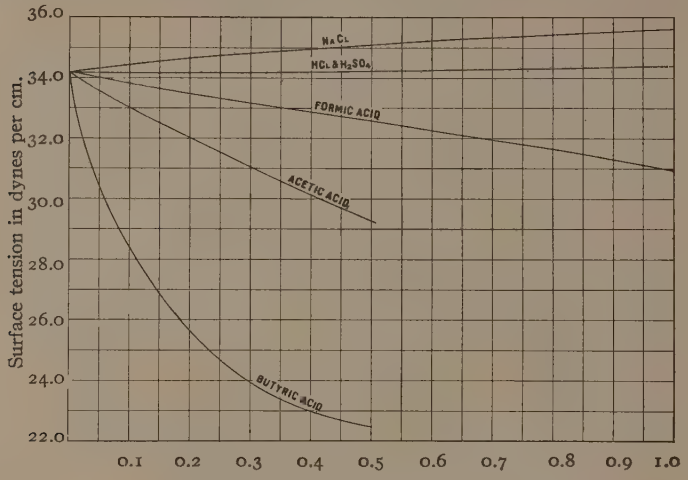

Fig. 5.—Surface tensions at the interface: Aqueous solution—Benzene.

but when different solutions of the base are used, or when the solution has been allowed to stand for some time, the results vary. The capillary-tube method as used by von Lerch,[1] is extremely inaccurate when a highly ionized base is present in the aqueous phase. The work upon the strong bases is still incomplete, and the data obtained will be reserved until later.

TABLE II.—WATER SOLUTION—BENZENE.

Hydrochloric Acid.

Conc., normal.....	0.000	0.0049	0.0098	0.0492	0.0980	0.987
Surface tension	34.18	34.22	34.21	34.17	34.23	34.35

Sulphuric Acid.

Conc., normal.....	0.000	0.0122	0.0242	0.0604	0.1208	0.2416	0.604	1.208
Surface tension ...	34.18	34.16	34.17	34.15	34.15	34.18	34.29	34.39

Sodium Chloride.

Conc., normal.....	0.000	0.0061	0.0123	0.0614	0.1228	0.2507	0.5205	1.034
Surface tension...	34.18	34.21	34.25	34.33	34.49	34.75	34.99	35.67

[1] *Ann. Physik*, **9**, 434–41 (1902).

TABLE II (*continued*).

WATER SOLUTION—BENZENE.

Formic Acid.

Conc., normal.....	0.00	0.005	0.010	0.0505	0.101	0.1935	0.2525	0.5275	0.881
Surface tension....	34.18	34.19	34.22	34.01	33.84	33.46	33.32	32.49	31.39

Acetic Acid.

Conc., normal.....	0.000	0.103	0.492	0.1034	0.2068	0.508
Surface tension...	34.18	34.01	33.56	33.02	31.99	29.24

Butyric Acid.

Conc., normal.....	0.000	0.010	0.020	0.100	0.200	0.300	0.500
Surface tension...	34.18	33.01	32.17	28.37	25.63	23.89	22.45

WATER SOLUTION—BENZENE.

Ammonium Hydroxide.

Conc., normal.....	0.000	0.0078	0.390	0.780
Surface tension.....	34.18	34.00	33.25	32.83

Summary of Papers I, II, and III.

1. The capillary tube method of determining surface tension has been found to be inaccurate whenever aqueous solutions of bases are used, but the drop-weight method gives accurate results. The difference is due to the fact that in the capillary tube method the surface of the liquid is very small, which makes it very sensitive to the action of impurities. In this method too, there is always the doubt as to the magnitude of the contact angle. The surface of a drop such as is used in drop-weight determinations is, on the other hand, relatively large, and may also be formed very quickly, thus giving a fresh surface, and the theory of the form of the drop gives no indication that the angle of contact is dependent upon the material of the tip if the tip has the proper form.

2. Lohnstein's theory as to the form of the function which must be inserted in the equation giving the surface tension α in terms of the weight of the falling drop (W), has been tested experimentally at the interface between two liquids. This is an ideal method from the standpoint of the theory of the formation of the drop, since in a liquid the drop falls much more slowly than in a gas. Lohnstein calculated the values of the function of r/a in the equation $\alpha = W[2\pi r f(r/a)]$. When Lohnstein's values of the function are plotted together with the experimental values as in Fig. 1, it is seen that the two curves have exactly the same form, especially at the beginning of the curve where $f(r/a) = 1$, and $r/a = 0$. For the larger values of r/a the experimental curve is smooth, while the Lohnstein curve becomes sinuous. This sinuosity is probably the effect of a failure to carry the integrations to a sufficient completeness, which probably resulted from the extreme laboriousness of a complete calculation. Lohnstein's values are not accurate to a greater degree than 4%,

so they cannot be used as a basis for accurate work, but his work has the great value that it proves that such laws as that of Tate are only approximations. The experimental curve is undoubtedly more accurate than that of Lohnstein.

3. The surface tension curve is somewhat flat at the bottom, and Tate's law assumes that the horizontal tangent is the same as the curve. However, it can be seen from the form of the curve that other tangents can be drawn which approximate the curve as closely as that which is horizontal, so that on this basis laws could be formulated, each as good as that of Tate though not so simple, and as numerous as the tangents to the curve.

4. The correction curve found experimentally is lower than corresponds to the values given by Morgan. This does not mean that Morgan's drop weights are incorrect, but that the values of the surface tension as determined by Ramsay and Shields and other workers by the capillary tube method are too low, since these are the results used by Morgan for the determination of the constant of his equation.

5. The correction factor used in the determination of surface tension by the drop-weight method may be brought very close to the value one by the use of extremely narrow tips, as was done by Antonow, but this is very inadvisable, as his results show, since they vary by 8%.

6. A surface tension apparatus has been devised for the accurate determination of surface tension at a liquid-liquid interface. This apparatus is very simple to set up and easy to use. It can be used for the determination of the surface tension of a single liquid, but the apparatus described in the fourth paper of this series is better suited for this purpose. Another apparatus (Fig. 4), designed for the determination of the surface tension by the capillary tube method, is described. The tube which contained the large meniscus (Fig. 4*C*) was 10 cm. in diameter, and to check the results the large meniscus was made about 15 centimeters in a glass cylinder. By the use of such large tubes the most common error in capillary height measurements was avoided. The use of a very large lower meniscus, advocated by one of the writers at the Boston meeting of the American Chemical Society, in 1909, and also in this paper as read before the National Academy in December, 1914, is considered by Richards and Coombs to be responsible for a large part of the increase in the values of the surface tension which they find in their work as compared with the older work of Ramsay and Shields and other workers.

7. The surface tension has been determined at the interfaces between water and the following liquids: benzene, ethyl carbonate, dimethyl aniline, xylene, toluene, and hexane. The results at the interface water-benzene are about 6% higher than those obtained formerly by von Lerch or by Antonow. This is interesting in that it is a change in the same di-

rection as that found by Richards and Coombs for the surface tension of single liquids.

8. The effects of acids, bases and salts upon the surface tension at the water-benzene interface, have been studied, and the results are shown graphically in Fig. 5. The effect of bases is much smaller than was found by von Lerch, for example, the new results are in some cases as much as 35% higher than the older ones. The difference in the results is due to a change from the capillary tube to the drop-weight method.

I wish to express my sincere thanks to Dr. William D. Harkins, under whose direction the above investigation has been pursued, for the personal interest he has taken in the work, and for the valuable advice and assistance which he has given throughout its progress.